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Syntheses and Crystal Structures of Triangular Rhodium and Iridium Complexes with Triply Bridging Sulfido Ligands

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Reaction of $[MCp^*(NCMe)_3]^{2+}$ (M=Rh, Ir; Cp*=η^5-C_5Me_5) with Na_2S in MeCN affords $[(MCp^*)_3(\mu_3\text{-}S)_2]^{2+}$. X-Ray structural characterization of their BF_4 salts shows that they have equilateral triangle M_3 core with two triply bridging sulfido ligands on both sides of the M_3 plane. Cyclic voltammograms of the rhodium and iridium complexes in MeCN show three and two chemically reversible processes, respectively.

The S,S- bicapped triangular cobalt clusters with cyclopentadienyls are of current interest in possessing a unique electronic configuration and solid-state magnetic properties.$^{1)}$ $[(CoCp)_3(\mu_3\text{-}S)_2]$ (Cp=η^5-C_5H_5) was first prepared from $[CoCp(CO)_2]$ with $(t\text{-}BuN)_2S$ by Otsuka, Nakamura, and Yoshida in 1968,$^{2)}$ and then recently, $[(CoCp')_3(\mu_3\text{-}S)_2]$ (Cp'=η^5-C_5H_4Me) and its oxidized forms were obtained from $[CoCp'(CO)_2]$ with CS_2.$^{1a)}$ On other cobalt triad, Rh and Ir, no corresponding analogues have been discovered, although several similar reactions using $[(RhCp^*)_2(CO)_2]$ with S_8,$^{3)}$ $[RhCp(PPh_3)_2]$ with S_8,$^{4)}$ $[RhCp^*(Ph)(H)PMe_3]$ with CS_2,$^{5)}$ $[RhCp^*Cl(\mu_2\text{-}Cl)]_2$ with $(Me_3Si)_2S$,$^{6)}$ and $[IrCp^*(SH)PMe_3(Cl)]$ with $(Me_3Si)_2NLi^{7)}$ have been attempted to date. We have found a convenient synthetic method to prepare $[(MCp^*)_3(\mu_3\text{-}S)_2]^{2+}$ (M=Rh, Ir) from $[MCp^*(NCMe)_3]^{2+}$ and Na_2S. Here we report on the synthesis and X-ray structural analysis of the triangular 48-electron dication.

$[(RhCp^*)_3(\mu_3\text{-}S)_2](BPh_4)_2$ (**1**) was synthesized as follows; a mixture of $[RhCp^*Cl(\mu_2\text{-}Cl)]_2{}^{8)}$ (556 mg) and AgOTf (925 mg) (OTf=O_3SCF_3) was stirred in MeCN (50 cm^3) for 30 min. A white precipitate of AgCl was removed from the mixture and the filtrate containing $[RhCp^*(NCMe)_3]^{2+8)}$ was added to a suspension of $Na_2S{\bullet}9H_2O$ (410 mg) in MeCN (100 cm^3). After stirring for 2 h, the reaction mixture was filtered to remove a black precipitate. The filtrate was treated with $NaBPh_4$ (580 mg) in MeCN (30 cm^3) and evaporated to dryness under a reduced pressure. The remaining solid was washed with CH_2Cl_2-MeOH (2:1). The solid was recrystallized from Me_2CO-MeOH (5:1) to give **1**$^{9)}$ as brown microcrystals in a 33% yield based on Rh. $[(RhCp^*)_3(\mu_3\text{-}S)_2](BF_4)_2$ (**2**)$^{10)}$ was obtained from **1** by replacement of BPh_4^- with BF_4^- of Ph_4PBF_4 in a 89% yield. It was recrystallized from CH_2Cl_2-C_6H_6 to give dark orange crystals used for structural characterization.

$[(IrCp^*)_3(\mu_3\text{-}S)_2](BPh_4)_2$ (**3**)$^{11)}$ or $[(IrCp^*)_3(\mu_3\text{-}S)_2](BF_4)_2$ (**4**)$^{12)}$ was prepared in a 28% or 90% (from **3**) yield in a similar manner using $[IrCp^*Cl(\mu_2\text{-}Cl)]_2{}^{8)}$ or **3** and Ph_4PBF_4. Compound **4** was recrystallized from Me_2CO. Both **1** and **3** are soluble in Me_2CO, MeCN and $MeNO_2$, while **2** and **4** are amphiphilic, and are soluble in water and in organic solvents such as CH_2Cl_2 and MeCN. The reactions are not straightforward and give messy products: reaction mixtures show many methyl proton signals from the Cp* groups in the ^{1}H NMR spectra between δ=1.5—2.3. Isolation of $[(\mathrm{MCp^*})_3(\mu_3\text{-S})_2]^{2+}$ is nevertheless easy because only its $\mathrm{BPh_4}$ salt is less soluble in $\mathrm{CH_2Cl_2}$ and MeOH as compared with many other unknown products. It is worthwhile to note that the triangular framework is also assembled directly by using the M(III) ions of $[\mathrm{MCp^*(NCMe)_3}]^{2+}$ (M=Rh, Ir) instead of the M(I) ions applied for the synthesis of $[(\mathrm{CoCp})_3(\mu_3\text{-S})_2]$.[2)]

X-Ray structural analyses of **2**[13)] and **4**[14)] reveal that they are isostructural and contain an equilateral triangle framework of three metal atoms capped on both faces by two μ_3-S atoms. The $\mathrm{M_3S_2}$ core has a D_{3h} symmetry similar to that of $[(\mathrm{CoCp'})_3(\mu_3\text{-S})_2]^{2+}$[1a)] as shown in Fig. 1 for **2**. Selected bond distances and angles are tabulated in Table 1. There is no significant difference between **2** and **4** . The Rh–Rh distance (2.830(2) Å) in **2** and the Ir–Ir one (2.832(1) Å) in **4** are in the ranges of the corresponding metal–metal single bond length in other complexes (2.70—2.87 Å for Rh-Rh, 2.65—3.09 Å for Ir-Ir).[15)] Each of **2** and **4** possesses 48 valence electrons that are needed for a metal triangle with three single bonds.[16)] The Rh–S (2.285(2) Å) and Ir–S (2.289(3)Å) distances are shorter and the M–S–M angles in **2** (76.5(1)°) and **4** (76.4(1)°) are smaller than those in the other triangular sulfido complexes (the M–S distances: 2.29—2.45 Å for rhodium complexes, 2.31—2.40 Å for iridium ones; the M–S–M angles: 78.19(7)—82.5(1)° for each complex) such as $[\mathrm{Ph_4P}][\mathrm{Rh_3}(\mu_3\text{-S})_2(\mathrm{CO})_6]$,[15a)] $[\mathrm{Rh_3(H)}(\mu_3\text{-S})_2(\mathrm{COD})_3]$,[15b)] $[\mathrm{Me_3(PhCH_2)N}][\mathrm{Ir_3}(\mu_3\text{-S})_2(\mathrm{CO})_6]$,[15c)] $[\mathrm{Ir_3(H)}(\mu_3\text{-S})_2(\mathrm{COD})_2(t\text{-}\mathrm{Bu_2PH})_2]$ (COD=η^4-1,5-cyclooctadiene).[15d)]

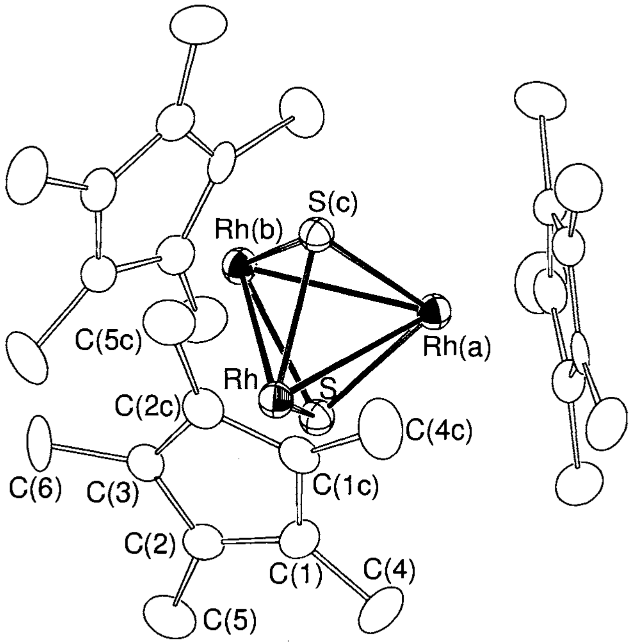

Fig. 1. ORTEP drawing of **2** showing 50% probability ellipsoids. A three-fold axis and a mirror plane pass through atoms S, S(c) and Rh, Rh(a), Rh(b), respectively.

The cyclic voltammogram of **2**[17)] with the 48-electron configuration reveals that it undergoes three chemically reversible reductions to form in turn the 49-electron monocation, 50-electron neutral molecule, and 51-electron monoanion. This electrochemical behavior is similar to that observed in $[(\mathrm{CoCp})_3(\mu_3\text{-S})_2]$[1d)] and $[(\mathrm{CoCp'})_3(\mu_3\text{-S})_2]$.[1a)] On the other hand, only two reversible reductions forming 49- and 50-electron complexes were observed for **4**[18)] in the same solvent.

Table 1. Selected bond distances (Å) and angles (°) of **2** and **4**

	2	**4**
M–M	2.830(2)	2.832(1)
M–S	2.285(2)	2.289(3)
M–C(1)	2.185(9)	2.19(1)
M–C(2)	2.195(7)	2.219(9)
M–C(3)	2.20(1)	2.22(1)
M–S–M	76.5(1)	76.4(1)
S–M–S	88.69(8)	88.9(1)

Intriguingly, the 49-electron species of the Ir complex is much unstable thermodynamically as compared with that of the Rh complex because the difference of the half potentials between 48e/49e and 50e/49e waves in the Ir complex ($\Delta E_{1/2}$=0.19 V) is much smaller than that in the Rh complex ($\Delta E_{1/2}$=0.40 V).[19]

In order to elucidate the electronic and magnetic behaviors and to compare with the cobalt triad triangular complexes, we are now trying to isolate a series of 50/49/48-electron complexes analogous to that in the cobalt triangular complexes[1] by chemical reduction of **2** or **4**, or by using M(III) and/or M(I) complexes (M=Rh, Ir) as starting materials.

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9) Characterization of **1**: Anal. Found: C, 65.55; H, 6.03%. Calcd for $C_{78}H_{85}B_2Rh_3S_2$: C, 66.12; H, 6.05%. FAB-MS: *m/z* 778 for $[M]^+$, 389 for $[M]^{2+}$. ^{1}H NMR (CD_3NO_2, 23 °C, TMS): δ 7.32—7.37 (m, BPh_4, 16H), 7.00 (t, $J_{H\text{-}H}$=7.4 Hz, BPh_4, 16H), 6.84 (t, $J_{H\text{-}H}$=7.2 Hz, BPh_4, 8H), 2.07 (s, C_5Me_5, 45H). ^{13}C NMR (CD_3NO_2, 23 °C, TMS): δ 165.4 (quar, $J_{C\text{-}B}$=49 Hz, BPh_4), 137.2 (s, BPh_4), 127.1 (quar, $J_{C\text{-}B}$=3 Hz, BPh_4), 123.3 (s, BPh_4), 107.8 (m, C_5Me_5), 11.8 (s, C_5Me_5). ^{103}Rh NMR (CD_3NO_2, 23 °C, references used $\Xi(^{103}Rh)$=12.6 MHz): δ 1323 (s).

10) Characterization of **2**: Anal. Found: C, 37.58; H, 4.60%. Calcd for $C_{30}H_{45}B_2F_8Rh_3S_2$: C, 37.84; H, 4.76%. FAB-MS: *m/z* 865 for $[M(BF_4)]^+$, 778 for $[M]^+$, 389 for $[M]^{2+}$. ^1H NMR (CD_3NO_2, 23 °C, TMS): δ 2.09 (s, C_5Me_5, 45H). ^{13}C NMR (CD_3NO_2, 23 °C, TMS): δ 107.8 (m, C_5Me_5), 11.8 (s, $C_5\mathit{Me}_5$).

11) Characterization of **3**: Anal. Found: C, 54.78; H, 5.09%. Calcd for $C_{78}H_{85}B_2Ir_3S_2$: C, 55.60; H, 5.08%. FAB-MS: *m/z* 1046 for $[M]^+$, 523 for $[M]^{2+}$. ^1H NMR (CD_3NO_2, 23 °C, TMS): δ 7.32—7.37 (m, BPh_4, 16H), 7.00 (t, $J_{H\text{-}H}$=7.4 Hz, BPh_4, 16H), 6.84 (t, $J_{H\text{-}H}$=6.5 Hz, BPh_4, 8H), 2.36 (s, C_5Me_5, 45H). ^{13}C NMR (CD_3NO_2, 23 °C, TMS): δ 165.4 (quar, $J_{C\text{-}B}$=49 Hz, BPh_4), 137.3 (s, BPh_4), 127.1 (quar, $J_{C\text{-}B}$=3 Hz, BPh_4), 123.3 (s, BPh_4), 101.9 (s, C_5Me_5), 11.4 (s, $C_5\mathit{Me}_5$).

12) Characterization of **4**: Anal. Found: C, 29.54; H, 3.69%. Calcd for $C_{30}H_{45}B_2F_8Ir_3S_2$: C, 29.53; H, 3.72%. FAB-MS: *m/z* 1133 for $[M(BF_4)]^+$, 1046 for $[M]^+$, 523 for $[M]^{2+}$. ^1H NMR (CD_3NO_2, 23 °C, TMS): δ 2.38 (s, C_5Me_5, 45H). ^{13}C NMR (CD_3NO_2, 23 °C, TMS): δ 101.9 (s, C_5Me_5), 11.4 (s, $C_5\mathit{Me}_5$).

13) Crystallographic data for **2**: $C_{30}H_{45}B_2F_8Rh_3S_2$, Mw=952.13, hexagonal, space group $P6_3/m$ (No. 176), a=11.412(1), c=15.746(1) Å, V=1775.8(5)Å^3, Z=2, μ(Mo$K\alpha$)=1.56 mm^{-1}, D_m=1.78 Mg m^{-3}, D_x =1.781 Mg m^{-3}. Intensity data ($|F_o| \geq 3\sigma(|F_o|)$) were collected on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo$K\alpha$ radiation λ=0.71073 in the $2\theta \leq 60°$ range at 296 K. The structure was solved and refined by using the Xtal 3.2 program. The current R value is 0.056 (R_w=0.059) for 1010 independent absorption-corrected reflections by Gaussian method (W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957)).

14) Crystallographic data for **4**: $C_{30}H_{45}B_2F_8Ir_3S_2$, Mw=1220.07, hexagonal, space group $P6_3/m$ (No. 176), a=11.419(1), c=15.753(2) Å, V=1779.1(5)Å^3, Z=2, μ(Mo$K\alpha$)=11.37 mm^{-1}, D_m=2.27 Mg m^{-3}, D_x =2.278 Mg m^{-3}. Intensity data ($|F_o| \geq 3\sigma(|F_o|)$) were collected on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo$K\alpha$ radiation λ=0.71073 in the $2\theta \leq 60°$ range at 296 K. The structure was solved and refined by using the Xtal 3.2 program. The current R value is 0.047 (R_w=0.047) for 1136 independent absorption-corrected reflections by Gaussian method as mentioned above.

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17) Electrochemical data of **2**: The half-wave potentials ($E_{1/2}$ vs Fc^+/Fc) in MeCN at a scan rate of 100 mV/s are as follows: 2+ → 1+, $E_{1/2}$=-0.90 V; 1+ → 0, $E_{1/2}$=-1.30 V; 0 → 1-, $E_{1/2}$=-2.56 V.

18) Electrochemical data of **4**: $E_{1/2}$ vs Fc^+/Fc in MeCN at a scan rate of 100 mV/s are as follows: 2+ → 1+, $E_{1/2}$=-1.21V; 1+ → 0, $E_{1/2}$=-1.40 V.

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